THE PRINCIPAL IDEAS IN THE INTERIONIC ATTRACTION THEORY OF STRONG ELECTROLYTES†

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INTRODUCTION

THE nature of electrolytic solutions is unquestionably one of the principal objects of study in modern physics and physical chemistry. Two different kinds of electrolytes, the weak and the strong, must be considered. The degree of dissociation in weak electrolytes is small in comparison with unity; that for strong electrolytes is nearly equal to unity. It is clear that we have often to deal with practically all transition types for which the degree of dissociation lies between zero and unity. For instance, this case is realized in more concentrated solutions. Furthermore, the definition of a weak and strong electrolyte is also dependent on the nature of the solvent. An electrolyte which is strongly dissociated when water is the solvent may be only weakly dissociated when, for example, benzene is the solvent.

The classical theory of Arrhenius is valid for the weak electrolytes; in this case the fundamental forces are the chemical or quantum-mechanics forces between the ions, which are significant for the chemical equilibria. From this quantum-mechanics point of view, it would be a very interesting problem to explain the dissociation constant in the law of Guldberg-Waage. The other limiting theory is the theory of Milner-Debye[1] which is valid in the case of strong electrolytes; here the ordinary Coulomb forces between the ions are of great importance. This modern electrostatic theory is applicable in the case of sufficiently dilute solutions and gives the quantitative limiting laws of the

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[1] S. R. Milner, Phil. Mag. (6) **23**, 551 (1912); **25**, 742 (1913); **35**, 214, 352 (1918). Transac. Faraday Soc. **15**, 148 (1919). P. Debye, Handelingen van het XIX e Nederlandsch Natuur—en Genees-kundig Congres. April 1923, te Maastricht. P. Debye and E. Hückel, Phys. Zeits. **24**, 185 (1923). See the following reviews: E. Hückel, Ergebn. d. exakten Naturwissenschaften **3**, 199ff. (1924). W. Orthmann, **6**, 155ff. (1927). E. Baars. Handb. d. Physik von Geiger—Scheel. XIII. 397–516, 1928. V. K. LaMer, Trans. Am. Electrochem. Soc. **41**, 507 (1927). A. A. Noyes, Journ. Am. Chem. Soc. **46**, 1080, 1098 (1924). Trans. Faraday Soc. Symposium on strong electrolytes, April 1927, 334–544, and "die Referate über die Struktur elektrolytischer Lösungen während der 90. Versammlung Deutscher Naturforscher und Ärzte in Hamburg" von M. Wien, G. Joos und E. Lange. Phys. Zeits. **29**, 751ff. (1928). See also the reviews by Ulich und Birr, Zeits. f. angewandte Chemie **41**, 443ff. 467ff. 1075ff. (1928). K. Förster ibid. **41**, 1013 (1928). N. Bjerrum. Ber. dtsch. chem. Ges. **62**, 1091 (1929) and H. Falkenhagen. Chemiker Kalender III. 346ff. (1931) and the forthcoming monograph, "Theorie der Elektrolyte" by H. Falkenhagen, Leipzig, S. Hirzel. (1931). The English translation will appear in the series of monographs edited by Prof. R. H. Fowler (Cambridge, England). Many references are also found in H. S. Taylor, "A Treatise on Physical Chemistry," New York, D. van Nostrand Company, (1931), and in the symposium on non-aqueous solutions. Chem. Rev. **8**, 167–352 (1931).

reversible thermodynamic and of the irreversible phenomena. The experimental results are generally in agreement with this theory. The Milner-Debye theory gives a theoretical explanation of the empirical laws developed by G. N. Lewis,[2] namely, that the activity coefficient in this limiting case depends only upon the square root of the concentration, and in case of mixtures of strong electrolytes, on the ionic strength of the solution. The ionic strength of a solution is defined by the expression

$$I = \tfrac{1}{2} \sum_i \gamma_i z_i^2$$

where γ_i is the concentration of the ions of the ith kind in moles per liter of solution, and z_i is the valence of an ion of the ith kind.

For the anomalous behaviour of strong electrolytes, that is, those that deviate from the ideal state, G. N. Lewis discovered this very important thermodynamic quantity called the activity, which has to be introduced in all thermodynamical laws instead of the usual expression for concentrations. Furthermore, the Debye theory shows that the square-root law for the electrical conduction, as a function of the concentration found experimentally by Kohlrausch, explains the change in the electrical conductance of dilute solutions of electrolytes with the concentration. Debye and Falkenhagen have also been able to show that these ideas have led to the prediction of an electrical conductance and a dielectric constant which are dependent on the frequency used in making the measurements. Later this effect was quantitatively verified by Sack, Zahn, Rieckhoff, Deubner, and co-workers, and M. Wien. Recently Falkenhagen has given a theoretical explanation of the dependence of the electrical conductance on the electric field found by M. Wien for all strengths and also of the viscosity phenomena. It is the purpose of this paper to show this recent development of the electrostatic Debye theory. Before we discuss these investigations, it is necessary to consider the fundamental ideas that underlie this new theory.

The Significant Ideas of the Debye Theory

In the first place Coulomb's law is used and measures the forces between the ions; these forces are inversely proportional to the square of the distance between the ions. The consequence of these forces is that a completely random distribution of ions in an electrolyte is impossible. The probability that two oppositely charged ions will come near to each other is greater than the probability that like charged ions will find themselves in the same position. To illustrate, let us assume a straight line of length r (of the order of magnitude $10^{-5} - 10^{-7}$ cm) around a certain ion, which for instance may be regarded as a positive ion. This ion may be at one end of the radius vector and an element of volume dS may be at the other end. When the electric charge in this

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[2] G. N. Lewis. Proc. Am. Acad. **43,** 259 (1907). Zeits. f. physik. Chemic **61,** 129 (1907); **70,** 212 (1909). G. N. Lewis and M. Randall. Thermodynamics and the free energy of chemical substances. McGraw-Hill Book Co., New York, 1923. Translated into German by O. Redlich, 1927. J. N. Brönsted, Journ. Amer. Chem. Soc. **42,** 761 (1920); **44,** 938 (1922); **48,** 2015 (1926). Further references see (1).

volume element is observed it will sometimes be found to be a positive charge, sometimes a negative charge. The time integral of this charge divided by the time of observation gives the mean charge. The result of the observation is that this mean electrical charge around the positive central ion is negative. It is assumed that this time of observation is great in comparison to the time of the Brownian movements which are of the order of magnitude 10^{-12} sec. The mean charge of the volume element dS divided by dS is called the electric density. This density is, in the case under consideration, negative. The probability of finding a negative ion around the central ion at a certain distance is greater than the probability of finding a positive ion at this same distance. This is a logical consequence of the Boltzmann principle. The result of this principle is a binding of negative ions to the positive central ion; this arises from the Coulomb forces between the ions in connection with the statistical interpretation in the sense of Boltzmann. The
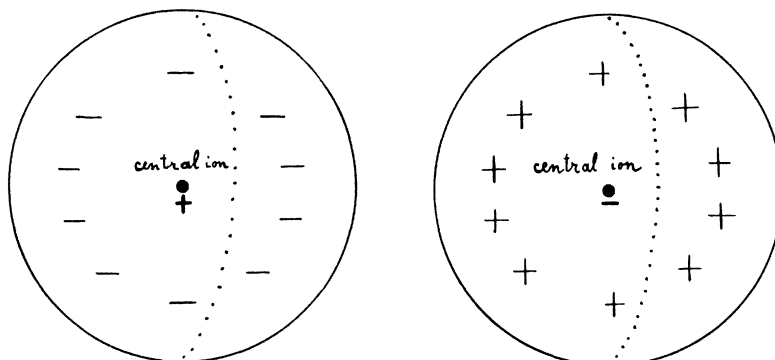

Fig. 1. Symmetrical distribution of the electric charge around a positive and a negative ion. "Centrally symmetrical ionic atmosphere."

space around the positive ion is called the negative "ionic atmosphere"; in the same way it can be understood that a negative ion is surrounded by a positive "ionic atmosphere." The density in the ionic atmosphere is of opposite sign to the charge carried by the central ion. The total charge of this atmosphere is equal and opposite to the total charge of the central ion (see Fig. 1). The ionic atmosphere has a definite "thickness" and in addition requires a certain time for its formation which is called the "time of relaxation." It can be shown that the electric density in the ionic atmosphere decreases with the distance according to the function $e^{-\kappa r}/r$ where κ has the dimension of a reciprocal length and is given by the formula

$$\kappa^2 = \frac{4\pi}{DkT} \sum_i n_i e_i^2.$$

where D is the dielectric constant of the solvent; k, Boltzmann's constant $(1.37 \times 10^{-16}$ erg/degree); T, absolute temperature; n_i, number of the ions of the ith kind in 1 cm^3; e_i, charge on ion of the ith kind and z_i, the valence of ion of ith sort $(z_i > 0)$. The thickness of the ionic atmosphere is $1/\kappa$, where

$$\frac{1}{\kappa} = 2.8 \times 10^{-10} \left(\frac{DT}{2I}\right)^{1/2} \text{cm}.$$

In the case of a simple electrolyte the thickness of the ionic atmosphere can be written

$$\frac{1}{\kappa} = \left(\frac{DT}{\gamma}\right)^{1/2} \frac{2.8 \times 10^{-10}}{(\nu_1 z_1^2 + \nu_2 z_2^2)^{1/2}} \text{cm}$$

where ν_1 and ν_2 are the dissociation numbers of the ions of a single molecule and γ is the concentration of the electrolyte in moles per liter of solution. The order of magnitude of $1/\kappa$ in centimeters is

$$\frac{1}{\kappa} \sim \frac{10^{-8}}{\gamma^{1/2}} \text{cm}.$$

The thickness of the ionic atmosphere is dependent in a definite manner on the valences of the ions, the temperature, the dielectric constant of the solvent and the ionic strength, according to Lewis. This property of the ionic atmosphere is important in a consideration of the reversible thermodynamic processes of strong electrolytes, for instance, the thermodynamic limiting law for the osmotic pressure, the freezing point depression, and the electromotive forces. It is also significant for the general thermodynamic quantity, the activity coefficient of an electrolyte, on which the above quantities are dependent. The thermodynamic limiting laws have been calculated by Debye and Hückel;[1] they agree generally with the experimental results, which were given by G. N. Lewis a considerable time in advance of the Debye theory.

The Table I gives the values of the thickness in centimeters for $\gamma = 0.0001$ and $\gamma = 0.001$ in water at 18°C. The characteristic dependence of the thickness of the ionic atmosphere on the concentration which follows the law $\gamma^{-1/2}$ is an

TABLE I. *Thickness of the ionic atmosphere. Solvent H_2O; 18°C.*

Type of electrolyte	$\gamma = 0.0001$	$\gamma = 0.001$
1-1	3.06×10^{-6} cm	0.97×10^{-6} cm
1-2	1.77 "	0.56 "
2-2	1.53 "	0.48 "
1-3	1.25 "	0.40 "
1-4	0.96 "	0.30 "
2-4	0.88 "	0.28 "

explanation of the proportionality of the change of the logarithm of the activity coefficient with the square root of the concentration and with the square root of the ionic strength in case of mixtures, as was found by G. N. Lewis, Randall and co-workers, and also by Brönsted.[1,2]

The second important property of the ionic atmosphere is the "time of relaxation," which was calculated by Debye and Falkenhagen.[3] The ionic atmosphere can neither be destroyed nor created in an infinitely small time in-

[3] P. Debye and H. Falkenhagen, Phys. Zeits. **29**, 121, 401 (1928).

terval. If an ion is suddenly removed from the solution the regularity represented by its ionic atmosphere will cease to exist, for the central force field of the central ion has disappeared. The result of this removal of the central ion is that the distribution of the charges of the ionic atmosphere to a random distribution with respect to the point where the central ion was, will take place gradually. The disappearance of this equilibrium position has been given mathematically by Debye and Falkenhagen.[3]

In this paper the irregular motion of the ions due to their Brownian movement was not considered quantitatively. Therefore, this first calculation was only qualitative. Debye gave the exact calculation[4] later in the special case
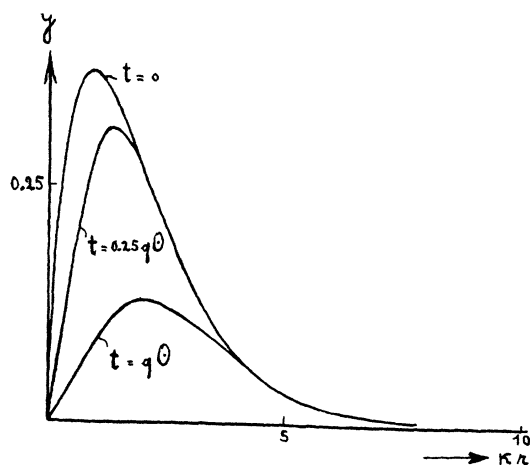

Fig. 2. y at different times. The quantity of electricity dQ which lies between spheres having radii r and $r+dr$ is: $dQ = -y\kappa e_i dr$; e_i = charge on ion of the ith kind; $1/\kappa$ = thickness of the ionic atmosphere; $q=0.5$ in the case of binary electrolytes; Θ = time of relaxation.

of binary electrolytes with ions of the same mobilities. Falkenhagen[5] was able to give the generalization in case of any simple electrolyte. The result of this calculation is given by means of a graph (see Fig. 2). For the quantity of electricity, dQ, which lies between spheres having radii r and $r+dr$, the following relation holds:

$$dQ = - y\kappa e_i dr$$

where e_i is the electric charge of the central ion

$$y = \kappa r e^{-\kappa r}\phi(\kappa r, \tau)$$

$$\phi(\kappa r, \tau) = \frac{1}{\pi^{1/2}} \int_{r^{1/2}-\kappa r/2r^{1/2}}^{\infty} e^{-x^2}dx$$

and $\tau = t/q\Theta$.

[4] P. Debye, Sommerfeld Festschrift, edited by P. Debye. "Probleme der modernen Physik." Leipzig S. Hirzel, 1928, p. 52.

[5] H. Falkenhagen, unpublished.

In this expression the time of relaxation Θ and q are given by the expression

$$\Theta = \frac{z_1 z_2}{z_2 l_1 + z_1 l_2} \frac{15.3 \times 10^{-8}}{kTq\kappa^2} \text{ sec}$$

$$q = \frac{z_1 z_2}{z_1 + z_2} \frac{l_1 + l_2}{z_2 l_1 + z_1 l_2} .$$

The l_i are the mobilies of the ions which are defined by the equivalent conductance Λ

$$\Lambda = \sum l_i$$

The quantity y is a measure of the density of the ionic atmosphere at different times and in a shell of thickness dr at different distances r from the ion in consideration. In Fig. 2 this quantity y is shown for $\tau = 0$, $\tau = 0.25$ and $\tau = 1$ as a function of κr. For each time y has a maximum value which decreases as κr is increased.

The quantity q has for $l_1 \gg l_2$ the limiting value $z_1/(z_1 + z_2)$ and for $l_1 \ll l_2$ the limiting value $z_2/(z_1 + z_2)$. Between these values q is a monotone function of l_1/l_2; in the case of binary electrolyte $q = 0.5$.

This Fig. 2 shows how the electric density in the ionic atmosphere at the time of the order of magnitude Θ is small compared with the original density at time zero. The time of relaxation Θ is a measure of the disappearance of the equilibrium condition. This time of relaxation is dependent not only on the concentration, the valence of the ions, the temperature and the dielectric constant of the solvent, but also on the mobilities of the ions. The order of magnitude of Θ is $10^{-10}/\gamma$ sec. in the case of a simple electrolyte. (See the values in Table II.) There have also been included in this table corresponding wave-lengths whose importance will be seen later, when we speak about the dispersion effect of the electrical conductance.

The properties of the ionic atmosphere "the thickness" and the "time of relaxation" are of great significance in a consideration of the irreversible conductivity processes of strong electrolytes and in the viscosity phenomena exhibited by strong electrolytes. We will illustrate this in the following paragraphs.

TABLE II. *Time of relaxation. Solvent water* ($\gamma = 0.001$)

Electrolyte	Θ	Corresponding wave-lengths
HCl	0.190×10^{-7} sec	5.7 m
KCl	0.553 "	16.6 "
LiCl	0.727 "	21.8 "
MgCl$_2$	0.323 "	9.7 "
H$_2$SO$_4$	0.094 "	2.8 "
CdSO$_4$	0.310 "	9.3 "
MgSO$_4$	0.315 "	9.5 "
LaCl$_3$	0.207 "	6.2 "
K$_4$Fe(CN)$_6$	0.103 "	3.1 "
Ca$_2$F$_e$(CN)$_6$	0.113 "	3.4 "

THE THEORY OF CONDUCTANCE IN THE STATIONARY CASE DEVELOPED BY DEBYE-HÜCKEL-ONSAGER[6]

It has been apparent that the ionic atmosphere is built symmetrically around an ion which is not exposed to external forces. If the ion is caused to move through the liquid with a certain velocity produced by an external electric field the ionic atmosphere cannot be symmetrical. The interionic forces tend to restore this symmetry, but as a consequence of the finite time of relaxation this symmetry is never completely restored; however, there will be built about each moving ion a stationary ionic atmosphere. This ionic atmosphere will be dissymmetrical in the direction of the motion of the ion. In front of the ion there will be more ions of like charge and behind it more ions of opposite charge than was the case when the ion was not moving (see Fig. 3). This dissymmetry of the electric density in the stationary case causes a force on the central ion which decreases its mobility. This force will be called the "electric force of relaxation."
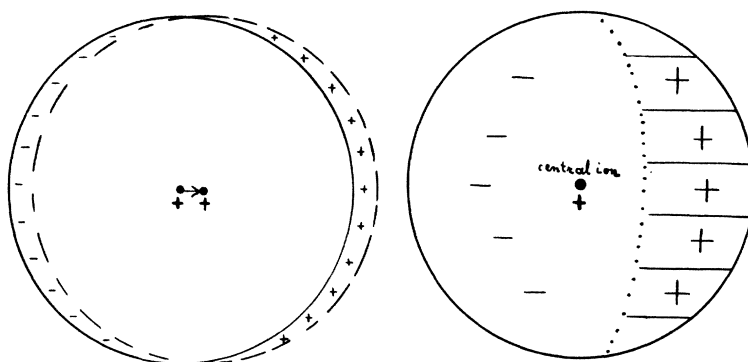
Fig. 3. Dissymmetrical distribution of the additional electric charge around a positive ion in the case of an external electric field.

The second reason for the decrease of the mobility of an ion is the electrophoretic effect. On account of the existence of a negative ionic atmosphere around a positive ion the electric field exerts a force on a volume element of this atmosphere and causes an additional movement of the solvent in the direction which is opposite to the external electric field; the result is, therefore, a frictional force, which is called the "electrophoretic force." Both forces are inversely proportional to the thickness of the ionic atmosphere; as the latter is inversely proportional to the square root of the concentration, the result is a decreasing mobility or conductance according to the square root law, which Kohlrausch had determined experimentally. According to this law the molar conductance of a strong electrolyte decreases with the concentration. This law holds only for very dilute aqueous solutions. The experimental verification of this law in non-aqueous solutions is more difficult, first, because the

[6] P. Debye and E. Hückel. Phys. Zeits. 24, 305 (1923). L. Onsager. Phys. Zeits. 28, 277 (1927). See also Trans. Faraday Soc. 1927. See also the Annual Reports Chem. Soc. London (1930) page 326.

experimental data are incomplete and unreliable; second, because the theory is applicable only when the electrolyte in solution is completely dissociated. In non-aqueous solvents the presence of undissociated molecules even in dilute solutions is a more common phenomenon than in aqueous solution. In spite of these difficulties Fraser and Hartley, Unmack, and other scientists[7] have shown that the square root law is satisfied by the conductance data for a number of uni-univalent salts dissolved in methyl-alcohol up to a concentration of $\gamma = 0.002$. They found in this case deviations for the solutions of higher valence types. The same difficulties with respect to the theory of Debye exist for the activity coefficient in non-aqueous solutions containing ions of the higher valence type found experimentally by Williams, Hansen and Williams.[8] It seems in this case the original assumptions in the Debye theory are to be modified. Long ago it was shown by Kahlenberg[29] that specific conditions often exist in this case.* This field cannot be discussed in detail at this time. It is preferable to take into consideration the principal applications of the original idea of Milner-Debye. The dispersion effect of the electric conductance and the dielectric constant discovered by Debye and Falkenhagen will be considered first.

The Frequency Dependence of the Electrical Conductance and of the Dielectric Constant (By Debye-Falkenhagen)[9]

If an ion is in motion there will be a dissymmetry of the ionic atmosphere which increases with an increase in the average velocity of the ions. An electric field which is changing with a certain frequency is assumed. For the ordinary frequencies the ionic atmosphere will have in each moment a dissymmetry of distribution of charges which corresponds to the momentary velocity of the ion. If the frequency is small in comparison with $1/\Theta$, a change of the electrical conductance will not occur. If the frequency is high in comparison with $1/\Theta$, the dissymmetry of the ionic atmosphere cannot be built up. This can be explained as follows: Imagine an ion, which is moving through the liquid with a constant velocity. It has been pointed out earlier that the ionic atmosphere around this ion must have a dissymmetrical electric charge. If the electric field is removed suddenly at the time $t = 0$, this dissymmetry will

[7] Fraser and Hartley. Proc. Roy. Soc. A109, 351 (1925). A. Unmack, Murray-Rust and Hartley, ibid. 127, 228 (1930). Further references in C. W. Davies. The Conductivity of Solutions. John Wiley and Sons, New York, 1930, and Chem. Rev. 8 (1931).

[8] J. W. Williams, Journ. Am. Chem. Soc. 51, 1112 (1929). Hansen and Williams, ibid. 52, 2759 (1930). J. W. Williams, Chem. Rev. 8, 303 (1931).

* For the detailed references see the recent work of Fredenhagen. Zeits. f. Physik. Chemie 152, 321, (1931) and the symposium on non-aqueous solutions. Chem. Rev. 8, 167–352, (1931). I am convinced that some of these questions will be cleared up by means of a detailed and generalized development of the ideas pointed out in the General Remarks p. (425) not only in the case of ions but also in the general case of particles, of which the solution consists.

[9] P. Debye and H. Falkenhagen. Phys. Zeits. 29, 401 (1928). Zeits. f. Elektroch. 34, 562 (1928). H. Falkenhagen, Forschungen und Fortschritte 4, 358 (1928). See also the following reviews: H. Falkenhagen and J. W. Williams Zeits. f. physik. Chem. A137, 399 (1928). Journ. of Phys. Chem. 33, 1121, (1929). Chem Rev. 6, 317 (1929).

disappear according to a law which is similar to the law that has been described in the case of the symmetrical distribution of charge. Falkenhagen has been able to calculate this non-stationary case[10] and has found that for this phenomenon the time of relaxation Θ must also be very important. The consequence of the latter consideration is that for sufficiently high frequencies the electrical conductance must be increasing; the electrical conductance is therefore dependent on the frequency of the electric field. This effect has been predicted by Debye and Falkenhagen and has been later verified by Sack, Zahn, Deubner, M. Wien and co-workers[11] in quantitative agreement with the theory.

Debye and Falkenhagen[9] have shown that the dielectric constant must also be a function of the frequency of the electric field and that it must be greater than the dielectric constant of the pure solvent and additionally also decreases with the frequency (see Fig. 4).* It is possible to explain this

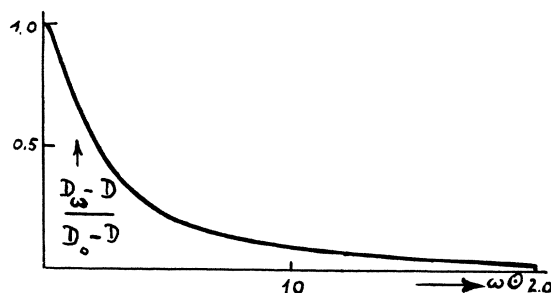Fig. 4. $D_\omega - D/D_0 - D$ as a function of $\omega\Theta \cdot \omega$ = frequency of the field; Θ = time of relaxation; D_ω = dielectric constant for the frequency ω; D_0 = dielectric constant for the frequency 0; D = dielectric constant of the solvent.

phenomenon in the following way. If an ion is periodically moved a phase difference is found between the electric field and the resulting velocity of the ion. The periodically changing electric field produces two components of the electric current; the first one is in phase with the field; the second one is in phase with the differential quotient of the field. This means a polarization displacement current in the sense of Maxwell-Faraday. The value of the latter is connected with the dielectric constant. That is the reason why an increase in the dielectric constant must be found. Only recently I received a

[10] H. Falkenhagen, unpublished.

[11] H. Sack, Phys. Zeits. **29**, 627 (1928). H. Sack. O. Mittelstaedt and B. Brendel, Phys. Zeits. **30**, 576 (1929). H. Sack and B. Brendel, Phys. Zeits. **31**, 345 (1930). B. Brendel, ibid. **31**, 822 (1930) and forthcoming Dissertation, Leipzig, 1931. H. Zahn, Zeits. f. Physik **51**, 350 (1928). H. Rieckhoff and H. Zahn, Zeits. f. Physik **53**, 619 (1929). H. Rieckhoff, Diss. Kiel. 1929; Ann. d. Physik **5**, 577, 1929. A. Deubner, Phys. Zeits. **30**, 946 (1929); Ann. d. Physik **5**, 305 (1930). S. Mizushima and H. Sack Phys. Zeits. **31**, 811 (1930). See also M. Wien, Phys. Zeits. **31**, 793 (1930); **32**, 183 (1931). See also Dissertation of B. Brendel Leipzig (1931) or B. Brendel, Phys. Zeits. **32**, 327 (1931).

* This curve is only qualitative; the quantitative formulas are developed in[9]; the detailed discussion will be published shortly in Phys. Zeits. by H. Falkenhagen and E. Vernon.

letter from Wien[12] wherein he stated that this predicted effect could be experimentally verified. Many scientists, as Walden, Ulich, Werner, Blüh, Schmick, Zahn, Sack, Pechhold, Skancke, Schreiner, Voigt, Fürth, and Deubner[13] have investigated about the dependence of the dielectric constant on the concentration. The measurements of these investigators showed very divergent results; some found a decrease, some no change; but none of them found the effect predicted by our theory. It is very interesting that the precise experimentation of M. Wien gave our predicted effect for the dielectric constant.

THE WIEN-EFFECT[14]

It is necessary to emphasize that the calculation of the dissymmetry can give an approximation only for small ionic velocities. This approximation is in the usual cases sufficient; but the case is different when one deals with the existence of extremely large ionic velocities produced by great field strengths, as has been done by Wien in his experiments. The velocity of the ions is of the order of magnitude of 1 meter per second contrasted to the usual velocities of the order of magnitude 0.01 mm/sec. In this case of high electric fields the ionic atmosphere can hardly be formed. It can be readily shown as has been done by Debye and Falkenhagen[9] that ions which have these high velocities will travel many times the thickness of their ionic atmosphere in the time of relaxation. Therefore, in abnormally strong electric fields the forces that have been termed the additional electrical force of relaxation and the electrophoretic force are of little or no significance and the conductance will approach the value found at infinite dilution. This deviation from Ohm's law is exactly the effect discovered experimentally by Wien and explains the beginning of the curve, conductance as a function of the electric field, by Joos and Blumentritt.[15] Recently Falkenhagen has given a calculation for the entire Wien curve, which is in agreement with the experimental results[16] and discussed this phenomenon with respect to the influence of the temperature, the valence, the dielectric constant and so on. In addition Falkenhagen found the explanation for the dispersion of the Wien effect which was

[12] M. Wien, forthcoming publication. See Phys. Zeits. **31**, 793 (1930); **32**, 183 (1931).

[13] P. Walden and U. Ulich, Zeits. f. physik Chem. **110**, 44 (1924). P. Walden u. O. Werner, Zeits. f. physik. Chem. **116**, 261 (1925). O. Blüh, Phys. Zeits. **25**, 220 (1924). H. Schmick, Zeits. f. Physik **24**, 56 (1924). H. Hellmann u. H. Zahn, Phys. Zeits. **27**, 636 (1926); Ann. d. Physik **81**, 711 (1926). H. Sack. Phys. Zeits. **27**, 206 (1926); **28**, 199 (1927). R. Pechhold. Ann. d. Physik **83**, 427 (1927). R. Fürth, Phys. Zeits. **25**, 676 (1924); **32**, 184 (1931). S. Skancke and E. Schreiner, Phys. Zeits. **28**, 597 (1927). B. Voigt, Zeits. f. Physik **44**, 70 (1927). A. Deubner, Ann. d. Physik **84**, 429 (1927).

[14] M. Wien, Ann. d. Physik **83**, 327 (1927); **85**, 795 (1928); s.a. Phys. Zeits. **29**, 751 (1928); Ann. d. Physik (5) **1**, 400 (1929). F. Bauer, Ann. d. Physik (5) **6**, 253 (1930). H. Possner, Ann. d. Physik (5) **6**, 875 (1930).

[15] G. Joos and M. Blumentritt, Phys. Zeits. **28**, 836 (1927). M. Blumentritt, Diss. Jena. Ann. d. Physik **85**, 812 (1928); ibid. (5) **1**, 195 (1929).

[16] H Falkenhagen, Phys. Zeits. **30**, 163 (1929), also Phys. Zeits. **32**, 353 (1931), and the forthcoming publication on the frequency dependence of the Wien effect, Phys. Zeits. (1932).

[17] F. Bauer, Ann. d. Physik (5) **6**, 253 (1930).

in agreement with the recently published results of Bauer[17] who has investi-
gated the influence of time on the Wien effect.

THE THEORY OF VISCOSITY (BY FALKENHAGEN)[18]

The investigations of Jones and Dole[19] suggested to me the problem of
studying the viscosity of strong electrolytes from the viewpoint of the elec-
trostatic theory. The properties of the ionic atmosphere make it also possible
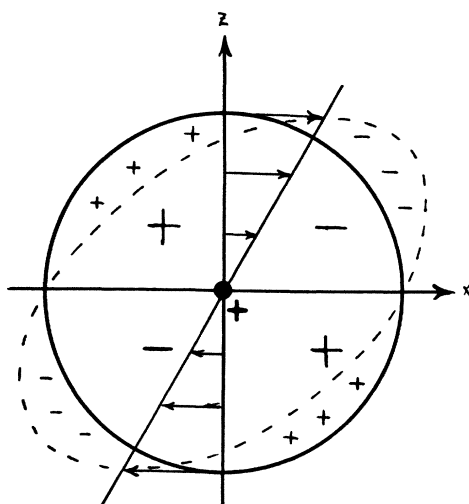

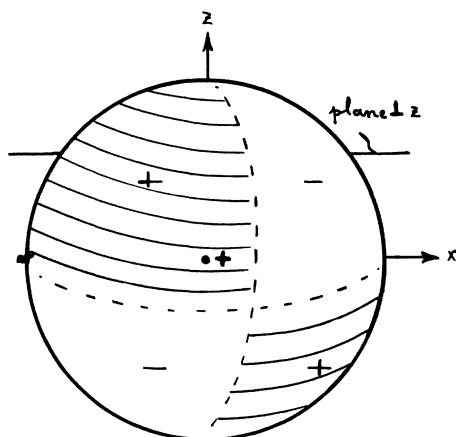Fig. 5. The deformation of the ionic atmosphere in the case of a velocity gradient.

Fig. 6. The distribution of the additional electric charge in the case of the viscosity.

to give an explanation of the irreversible mechanism that is involved in the
viscosity phenomena exhibited by strong electrolytes. To illustrate we might
consider the following case. Imagine a plane perpendicular to the axis along

[18] H. Falkenhagen and M. Dole. Phys. Zeits. 30, 611 (1929); Zeits. f. physik. Chem. B. 6,
159 (1929), also H. Falkenhagen, Phys. Zeits. 32, 365 (1931).
    [19] G. Jones and M. Dole, Journ. Amer. Chem. Soc. 51, 2950 (1929).

which the velocity of the ions is changing. The result of the velocity gradient is a deformation of the ionic atmosphere in the sense of Fig. 5. If we take into consideration the successive layers above the plane, we see that as a result of the electric lines of force coming from the added electric charge, a force is built up on the central ion parallel to the x-axis (see Fig. 6). The total shearing force which is produced over an area of one square centimeter lying perpendicular to the velocity gradient, can be calculated. In making this calculation the negative ions with their deformed ionic atmospheres must be also taken into consideration. In this case the distribution of the electric charge is complementary to the corresponding distribution of the charges in Fig. 6. This force is proportional to the velocity gradient. The proportionality factor is obtained by adding to the viscosity of the original solvent the effect due to the Coulomb forces existing between the ions.

If we call the viscosity of the electrolyte η_γ in molar concentration γ (in moles per liter) the viscosity of the pure solvent η_0, then Falkenhagen could theoretically derive[18] the following relation which holds (or is applicable) in case of dilute solutions.

$$\eta_\gamma = \eta_0(1 + A(\gamma)^{1/2})$$

In this expression A depends in a definite manner on the valence of the ion, its mobility, the absolute temperature, the dielectric constant and the viscosity of the pure solvent η_0 in the special case of binary electrolytes with ions of the same mobilities. For potassium chloride I obtained at 18°C, $A = 0.0046$ with water as solvent. Recently Joy and Wolfenden[20] have verified this predicted value experimentally.

In this connection it might be interesting to note that I have recently calculated the general expression for the viscosity of any simple strong electrolyte and that I have also derived the general limiting law for viscosity phenomena. The expression is the same as that indicated in the formula above excepting that the coefficient A is in this case additionally dependent in a much more complicated manner on the mobilities and valences of both ions. I shall not give the expression in detail at this time, for it will be published* shortly.[21] I have recently received a letter from Mr. Wolfenden wherein he kindly informed me that he has verified experimentally the value for HNO_3 predicted by me, $A = 0002$.

It would be very interesting to compare the theoretical results with systematic experimental studies, which will have to be performed in the future.† A systematic investigation of the viscosity of weak electrolytes as a function of concentration, etc., would also be very interesting. I believe that in this

[20] W. E. Joy and J. H. Wolfenden, Nature **126**, 994 (1930).

* I wish to thank Mr. E. Vernon (a student of Professor Farrington Daniels) for helping me with the theoretical discussion of this work.

[21] H. Falkenhagen. Forthcoming publications in Phys. Zeits. **32**, 1931; Zeits. f. physik. Chem. B. 1931; and H. Falkenhagen and E. Vernon, Journ. of Amer. Chem. Soc. 1931. See also H. Falkenhagen, Nature **127**, 439 (1931).

† I suggested such measurements to Professor J. W. Williams of the Physical Chemistry Department of the University of Wisconsin some time ago.

case the dependence of the viscosity on the concentration does not follow the square root law, but presumably is linear. These linear terms are also important for the more concentrated solutions of strong electrolytes. Perhaps it would be possible to develop further the exact differential equations pertaining to the problem so that this field may be explored. In doing this it will be necessary to take into consideration the relaxation effect of the dipole molecule of the solvent on the viscosity of the solution and the depolymerisation effect.‡ The first effect has recently been calculated by Finkelstein[22] according to whom this effect is proportional to the concentration. Although I am at present not fully convinced as to the validity of the values calculated by Finkelstein, it nevertheless appears that some interesting explanation of the structure of electrolytic solutions is to be expected by comparison with experimental results.

GENERAL REMARKS

One of the most interesting problems on the field of electrolytic solutions is the following. At the beginning of this paper the two limiting theories have been discussed, which explain the phenomena for the weak and strong electrolytes. In the case of the weak electrolytes only the quantum-mechanics forces, that is, the truly chemical forces are important.[23] In the case of the strong electrolytes the electrostatic Coulomb forces have the greatest importance. It would be very interesting, starting from these limiting theories, to develop an entirely satisfactory theory of the more concentrated solutions,which at present has not been worked out in spite of many attempts. I refer to the theories of Hückel, Bjerrum, Müller, Gronwall, Sandved, La Mer, Nernst, and so on.[24] These theories probably with the exception of the theory of Gronwall, La Mer and Sandved are only significant from an empirical point of view. It may be shown, starting from the statistical interpretation of the Debye theory given by Fowler and Kramers[25], that the theories mentioned cannot be entirely correct.

To this purpose it would be advisable to call attention to the exact statis-

‡ This effect is important in the case of the more concentrated solution and gives a negative *additive* viscosity.

[22] B. N. Finkelstein, Phys. Zeits. **31**, 130, 165 (1930).

[23] See for instance "Quantentheorie und Chemie," Leipziger Vorträge, 1928, edited by H. Falkenhagen. W. Heitler Phys. Zeits. **31**, 185 (1930).

[24] E. Hückel. Phys. Zeits. **26**, 93 (1925). H. Müller, Phys. Zeits. **28**, 324 (1927). T. H. Gronwall. V. K. La Mer und K. Sandved, Phys. Zeits. **29**, 358 (1928). L. J. Greiff, Dissert. New York, Columbia University, 1930. V. K. La Mer and R. G. Cook, J.A.C.S. **51**, 2622 (1929). La Mer and H. Goldman, J.A.C.S. **51**, 2632 (1929). La Mer and W. G. Parks, J.A.C.S. **53**, 2040 (1931), and La Mer and C. S. Mason, J.A.C.S. **49**,410 (1927). L. J. Greiff, Dissertation,New York, 1930. N. Bjerrum, Danske Vid. Selsk. Mat. Fys. Medd. **7**, Nr. 9, 1926. W. Nernst. Zeits. f. Elektroch. **428** (1927). W. Orthmann, Ergebn. d. exakt. Naturn. **6**, 155 (1927). S. M. Naudé, Zeits. f. Elektroch. 532 (1927). W. Nernst. Berl. Akad. Ber. **2**, 4 (1928); Zeits. f. physik. Chem. **135**, 237 (1928). W. Nernst. u. W. Orthmann, Zeits. f. physik. Chem. **135**, 199 (1928). S. M. Naudé, Zeits. f. physik. Chem. **135**, 209 (1928).

[25] R. H. Fowler. Trans. Faraday Soc. **23**, 434 (1927). See also the monograph of R. H. Fowler. Statistical Mechanics. Cambridge 1929. H. A. Kramers, Proc. Amsterdam **30**, 145 (1927.)

tical treatment of the problem of the electrolytic solutions given by Fowler and Kramers. These authors start from the phase integral, that is the distribution function of the potential energy, U, which controls the distribution of all particles in the solution. According to the statistical interpretation the free energy of the electrolyte can be written

$$F = - kTl_n \int \cdots \int e^{-U/kT} d\Omega$$

In this expression $\int \cdots \int$ means the state integral in the phase space. Kramers tried to find out the solution for this integral and could show that this integral is divergent and not dependent on the ionic diameters below a certain concentration. Furthermore, Kramers was able to show that one state of the statistical distribution is independent of the ionic size and is stable below this certain concentration which is in the case of uni-univalent electrolytes for water 0.03 mol. per liter, and in the case of bivalent electrolytes 0.0075 mol. per liter. This result of Kramer's possesses an interesting formal analogy to the results in the theory of Heisenberg[26] about ferromagnetism. It is well known that below the Curie-point a relatively simple formula exists for the dependence of the magnetic moment on the magnetic field and the Curie-constant is dependent rather simply on the interchanging integral. Below the Curie-point the matter is very complicated. It seems to be impossible to calculate the state integral if spontaneous magnetism exists. The behaviour of the strong electrolytes corresponds to the phenomenon of ferromagnetism. I am grateful to Prof. Kramers for this analogy.

It seems to be impossible to calculate the state integral above the mentioned critical concentration as long as one does not introduce the finite diameter of the ions. For concentrations below half of the "critical concentration" the development given by Kramers is valid and gives nearly the same result developed by Debye. Kramers formerly believed that this also is true when one considers the finite dimensions of the ions. This problem requires an extensive mathematical investigation wherein the statistical treatment employed by Kramers should be developed further by taking into consideration the finite dimension of the ions. From the results of this calculation the exactness of the treatment given by Gronwall, La Mer and Sandved can be determined. Perhaps it would be possible to develop a reasonable theory of more concentrated solutions when one combines the Kramer's theory and the theory of Bjerrum. The development of a more exact theory for concentrated solutions must take into consideration the following concept.*

All the authors mentioned above make use of the Coulomb forces between the ions. In reality not only the electrostatic forces (that is the Coulomb forces and the forces of polarization) are significant, but also the quantum-mechanics forces and the interionic dispersion forces are of great

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* These ideas are capable of a generalization in the case of particles, of which the solution consists and will presumably give an explanation of some phenomena found out experimentally also in non-aqueous solutions.

[26] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928).

moment. The latter correspond to the Van der Waals forces in the case of gases and are not only of electrostatic nature, but of quantum-mechanics nature as has been recently shown by London, Eisenschitz and Margenau.[27]

One of the most important problems is the ascertainment of the true degree of dissociation. All the questions mentioned above require considerable experimental investigation. For instance, it would be necessary to consider the absorption spectra, the Raman-effect,* the method for determination of the structure of a molecule recently worked out by Debye.[28] The structure of the electrolytic solutions is one of the most interesting problems of the future. In concluding I wish to thank Prof. P. Debye (Leipzig Germany) for the helpful counsel that he has given me for this manuscript and for his kindly interest. I am also indebted to Prof. V. K. La Mer and Prof. H. A. Kramers for helpful correspondence. Professor Karl Paul Link of the University of Wisconsin helped me very generously with the preparation of the manuscript and the proof reading.

[27] Eisenschitz u. London. Zeits. f. Physik **60**, 491 (1930). See also G. Podolanski, Phys. Zeits. **31**, 803 (1930). F. London. Zeits. f. Physik **63**, 245 (1930). H. Margenau, Zeits. f. Physik **64**, 584, (1930); Phys. Rev. **36**, 1782 (1930).

[28] For a detailed consideration see the forthcoming monograph of the author, reference (1).

[29] L. Kahlenberg, Journ. of Physical Chem. **3**, 12 (1899); L. Kahlenberg and H. Schlundt Journ. of Physical Chem. **6**, 447 (1902).

* See for instance the significant work of Rao and Woodward on the problem of the Raman effect and Dissociation in the case of nitric acid and sulfuric acid etc. R. Rao, Proc. Roy. Soc. **A127**, 279 (1930), see also E. L. Kinsey, Phys. Rev. **35**, 284 (1930); L. A. Woodward, Physik. Zeits. **31**, 792 (1930), **32**, 212, 261 (1931). Here see further references.